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New Data on the Velocity Distribution of H(2*S*) Atoms Produced by Dissociative Excitation of H_2†

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New structure has been observed in the time-of-flight distribution of H(2*S*) atoms produced by electron bombardment of H_2. The observed time-of-flight peaks are so located as to agree with the interpretation that the dissociative excitation proceeds predominantly through predissociation of intermediate bound states.

Metastable H(2*S*) atoms produced by electron bombardment of H_2 have been observed, by time-of-flight measurements,[1-3] to have kinetic energies large compared to those corresponding to the thermal motion of their parent molecules. These kinetic energies are grouped about two widely separated maxima at 0.32 and 4.7 eV.[1] Using target molecules at a temperature of about 80°K, the time-of-flight spectrum obtained in the present experiment is essentially the same as those reported previously; however, with target molecules at a temperature of about 50°K, the spectrum for the low-energy atoms splits into several peaks, as is demonstrated in Fig. 1. It will be shown that the spectrum of Fig. 1 can be decomposed into six or seven independent time-of-flight spectra, each having a form and width attributable to thermal motion of the target molecules and momentum transfer to them by the inelastically scattered electrons. This observation is consistent with the interpretation that the dissociative excitation observed here proceeds predominantly through predissociation of intermediate bound states. Specifically, by comparing the present time-of-flight spectra with previous observations of optical-absorption spectra,[4] photodissociation spectra,[5-7] and photoionization spectra,[8] it is concluded that the observed dissociative excitation proceeds almost exclusively

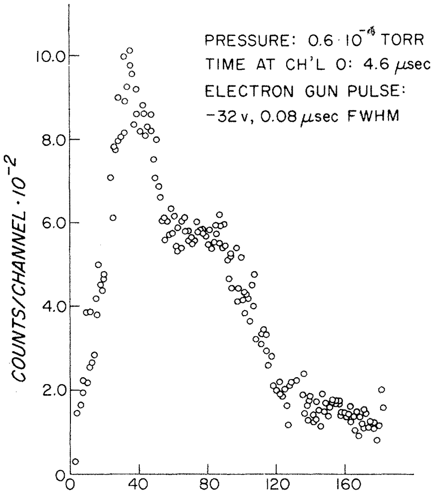

FIG. 1. Time-of-flight spectrum for H(2*S*) atoms from excited molecules having a temperature of about 50°K. These data are the difference between a total spectrum and a background spectrum obtained by measuring these signals in alternate 40-min intervals for a period of about 20 h. A few channels affected by identifiable spurious effects have been deleted from the spectrum.

through predissociation of one or more states in each of the seven groups of levels listed in the *sixth* column of Table I.

Predissociation in the $D\,^1\Pi_u$ levels of H_2 has been noted previously[4-7]; however, dissociation spectra attributable to predissociation of the three high-lying Rydberg levels listed in Table I have not been reported previously. The absence of these three peaks in optical-absorption spectra is probably due to the rapid decrease of absorption oscillator strength as the principal quantum number for the excited electron increases.

Before describing the experiment it is necessary to review the relation between the temperature of the target H_2 gas and the time-of-flight distribution for the H(2S) atoms. In this discussion it will be assumed that the H(2S) atoms are produced isotropically in the rest frame of their parent molecules. If the cross section for the production of H(2S) atoms were zero except at the threshold for dissociative excitation, and if momentum transfer by the inelastically scattered electrons were negligible, then the atoms would have a Maxwellian distribution of kinetic energy. Their time-of-flight distribution would be represented by

$$P(t) \propto t^{-4} \exp(-At^{-2}),$$

where $A = 2mL^2/kT$, L is the flight distance, and m is the mass of a hydrogen atom. For excitation to a discrete level lying above threshold, the kinetic-energy distribution has the form of a "distorted" Maxwellian curve,[10] and the speed distribution approaches a Gaussian shape in the limit

$$E_i \gg kT,$$

where E_i is one-half the difference between the discrete excitation energy and the threshold for dissociative excitation. In this limit

$$P(t) \propto \frac{1}{t^{-3}} \exp\left[-A\left(\frac{1}{t} - \frac{1}{t_i}\right)^2\right],$$

where $t_i = L(m/2E_i)^{1/2}$. Distributions which agree qualitatively with these forms can be seen in Fig. 1; there, the two peaks (barely resolved) near channel No. 40 are narrower than any peak occuring at a later time.

Resolution of the peaks observed in this experiment required that the temperature of the target gas be less than 60°K. This was ascertained by forming linear combinations of functions $P(t)$ at appropriate values of t_i from 7 to 16 μsec with various time separations between 1 and 3 μsec. This procedure was also used with the observed values of t_i to estimate that the low-temperature data (Fig. 1) was taken with excited molecules[11] at about 50°K.

The present arrangement of apparatus, depicted schematically in Fig. 2, is similar to that used by Leventhal, Robiscoe, and Lea.[1] The target H_2 gas is excited by a short burst of electrons, at $t = 0$, and H(2S) atoms are detected at a later time, t, at a distance L from the point

Table I. Location and identification of peaks in the H(2S) time-of-flight spectrum.

Location in time (μsec)	Channel number (Fig. 1)	H(2S) kinetic energy (eV)	Excitation energy (Å)	Optical absorption feature (Å)	Predissociating levels	Dissociation curves
8.4	35	0.86	753±4 [a]	753.3 [b] 755.6 [b]	$9p\sigma\,^1\Sigma_u^+$ ($v = 5$) $8p\sigma\,^1\Sigma_u^+$ ($v = 5$)	$(2s\sigma)(2p\sigma)\,^1\Sigma_u^+$
9.3	43	0.68	768±4	765.4 [b]	$8p\sigma\,^3\Sigma_u^+$ ($v = 4$)[d]	$(2s\sigma)(2p\sigma)\,^3\Sigma_u^+$
13.4	80	0.34	807±2	805 [c]	$D\,^1\Pi_u$ ($v = 6$)	$B'\,^1\Sigma_u^+$
15.4	98	0.26	817±1	816 [c]	$D\,^1\Pi_u$ ($v = 5$)	$B'\,^1\Sigma_u^+$
18.7	128	0.17	827±0.5	827 [c]	$D\,^1\Pi_u$ ($v = 4$)	$B'\,^1\Sigma_u^+$
21.3	152	0.13	830±0.5	839 [c]	$D\,^1\Pi_u$ ($v = 3$)	$B'\,^1\Sigma_u^+$

[a] These uncertainties are discussed in the text.

[b] Ref. 8. The first and third of these features are abnormally broad autoionization peaks; the second feature is a missing autoionization peak.

[c] Refs. 4-7. These features are peaks in both optical-absorption and photodissociation spectra.

[d] The triplet level listed here should be nearly degenerate with the singlet level observed in optical absorption. (Ref. 8). This tentative identification is made because the calculated (Ref. 9) energy separation between the two repulsive curves at the curve crossing position is approximately equal to one vibrational quantum, at this excitation energy.

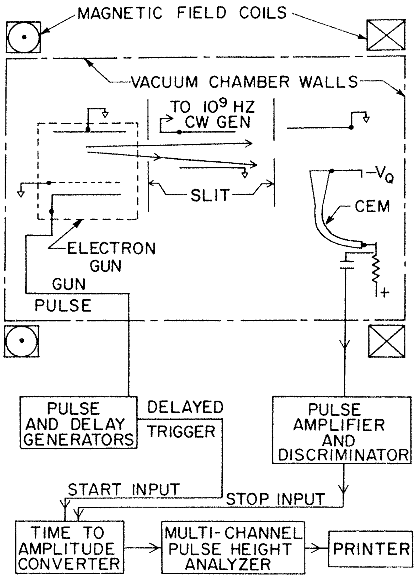

FIG. 2. Schematic diagram of the electronic apparatus.

of production. The distance L is approximately the same for all the atoms. The atoms are detected by quenching them in a dc electric field and observing the resultant Lyman-α radiation with a channel electron multiplier. With the electron gun pulsed at a repetition rate of about 30 kHz the H(2S) count rate is about one per second. A background signal, presumably due to atomic ions, is separated from the H(2S) signal by prequenching the metastable atoms in a small rf-field region, located approximately midway between the electron gun and the channel electron multiplier. The rf field is driven at the appropriate Lamb-shift frequency, 1.06 GHz.

The electron gun and detector are enclosed in a 2-liter stainless-steel can which is pumped continuously by a trapped, 2-in.-diam oil diffusion pump. The pressure at the detector is maintained a factor of 10 lower than that at electron gun by differential pumping through two collimating slits of 0.2 cm width and 1 cm length, which are 10 cm apart. The pressure at the electron gun was varied, for various sets of data, between 0.1×10^{-4} and 3.0×10^{-4} Torr.

A slow, steady gas flow through the vacuum system is maintained by leaking in research-grade hydrogen through a stainless-steel needle valve. The gas is cooled by expansion in the needle valve from room temperature and a pressure of about 15 atm to less than 50°K and a pressure of about 10^{-4} Torr. If the expansion were streamline and adiabatic the low-pressure gas would have a temperature of about 10°K. The gas temperature at the electron gun depends upon the flow impedance between the needle valve and the main vacuum chamber. The time-of-flight spectrum shown in Fig. 1 corresponds to minimization of this impedance, whereas spectra corresponding to excited molecules having a temperature of 80°K are obtained by connecting the needle valve to the main vacuum chamber through 30 cm of $\frac{1}{4}$-in.-i.d. stainless-steel tubing. A distribution with a full width at half-maximum 7% greater than that for the distribution associated with 80°K was obtained by inserting an additional 10-cm length of tubing packed with stainless-steel wire. Unfortunately, the configuration of the applied magnetic field was also different for this high-temperature run; thus, since the size and location of the excitation region is probably affected by this field, the only conclusion available is that the observation of a broader distribution admits the possibility that with this arrangement the excited molecules have a temperature greater than 80°K.

The lateral dimension of both the electron-gun cathode and the entrance aperture to the electron multiplier is about 0.2 cm, and the distance between them is about 11 cm; therefore, the spread in a time-of-flight peak due to variations in points of origin and quenching is about ±4%. The electron-gun pulse width was varied, for various runs, between 0.1 and 0.2 μsec, causing a broadening of about ±1% at a time-of-flight of 10 μsec. These instrumental effects, together with imperfect cooling of the target gas and variations in momentum transfer to the molecules during excitation, limited the resolution of the present time-of-flight spectra to that shown in Fig. 1.

The peaks listed in Table I were obtained from analysis of eight different time-of-flight spectra taken with the excited molecules at 50°K, and one spectrum with a temperature greater than 80°K. The uncertainty in each excitation energy listed in Table I was obtained by adding ±0.5 μsec, an approximate representation of possible systematic errors, to the largest observed deviation from the mean value for the corresponding time-of-flight peak.

The count rate near channel No. 60 in Fig. 1 is too high to be associated exclusively with the predissociation peaks at 9.3 and 13.4 μsec. This can be accounted for either by assuming that some of the H(2S) atoms result from direct excitation to the dissociation continuum, or by assuming that an unresolved predissociation peak is located near channel No. 60, at a time-of-flight between 10 and 12 μsec. In view of the prominence of the photodissociation peak near 795 Å,[5,7] due to predissociation in the $D\,^1\Pi_u$ ($v=7$) levels, and the identification in Fig. 1 of peaks due to predissociation in the $D\,^1\Pi_u$ ($v=3$, 4, 5, 6) levels, the latter interpretation is quite acceptable.

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[11] For the present discussion it suffices to treat momentum transfer to the target molecules by the incident electrons as an effect which causes the temperature of the excited molecules to be larger than that of the target gas as a whole; thus, a temperature which is determined from the analysis of time-of-flight spectra refers to excited molecules.